

## PATENT SPECIFICATION

NO DRAWINGS

1083,880



1083,880

Date of Application and filing Complete Specification: May 19, 1965.  
No. 21276/65.

Application made in United States of America (No. 371751) on June 1, 1964.

Application made in United States of America (No. 418271) on Dec. 14, 1964.

Application made in United States of America (No. 434092) on Feb. 19, 1965.

Application made in United States of America (No. 443638) on March 29, 1965

Complete Specification Published: Sept. 20, 1967.

© Crown Copyright 1967.

Index at acceptance: —C2 C(3A10A4C, 3A10A5G1, 3A10A5H, 3A10E1)

Int. Cl.: —C 07 c 51/14

## COMPLETE SPECIFICATION

### The Preparation of alpha,beta-ethylenically-unsaturated Carboxylic Acids and/or beta-acyloxy carboxylic Acids

We, UNION OIL COMPANY OF CALIFORNIA, a Corporation organised under the laws of the State of California, United States of America, of 461 South Boylston Street, Los Angeles, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the oxidative carbonylation of olefins to carboxylic acids and in particular to unsaturated carboxylic acids. In a specific embodiment, this invention relates to the oxidative carbonylation of ethylene to acrylic acid.

The unsaturated carboxylic acids such as acrylic acid are very attractive commercial commodities. The commercial preparation of the unsaturated acids and in particular acrylic acid, however, is quite complex and is based on relatively expensive raw materials. To illustrate, the raw materials presently employed for the preparation of acrylates or acrylic acid include acetylene, ethylene cyanohydrin, ketene and betapropiolactone. The chemistry involved in the preparation of acrylic acid and acrylates from the aforementioned raw materials is quite complex and high yields of the acid are not readily obtained. As a result, only a few manufacturers produce these chemicals and these producers enjoy a relatively stable price structure free from intensive competition with other chemistry.

It is an object of this invention to provide a method for the oxidation of olefins to carboxylic acids.

It is an object of this invention to provide

[Price 4s. 6d.]

a direct oxidation to acrylic acid from ethylene. 40

It is a further object of this invention to provide a continuous oxidation for the preparation of carboxylic acids from olefins.

Other and related objects will be apparent from the following description. 45

We have now found that alpha- beta-unsaturated carboxylic and beta-acyloxycarboxylic acids can be directly prepared by an oxidative carbonylation reaction. Our process comprises contacting an olefin, carbon monoxide and oxygen with an organic solvent containing a platinum group metal and, optionally, a redox agent. Beta-acyloxycarboxylic acids are also obtained and these can readily be pyrolyzed by thermal and/or catalytic processing to provide complete conversion to the alpha,beta-unsaturated carboxylic acids. 50 55

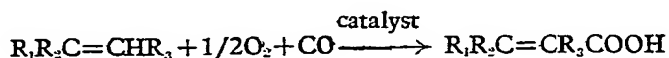
The invention also provides a reaction medium which contains acetic acid, a carboxylic acid having a boiling point in excess of the boiling point of said alpha, beta-ethylenically unsaturated acids and the anhydrides of said acids. 60 65

It has been reported that carbonylation of olefins can be performed with organic solvents containing a platinum group metal salt. To illustrate, it has been reported that ethylene, when contacted with a benzene solution of palladium dichloride and carbon monoxide forms beta-chloropropionyl chloride. This reaction, however, results in a stoichiometric reduction of the palladous ion to palladium metal. Accordingly, this reaction has heretofore remained a laboratory curiosity useful for proving reaction mechanisms but not offering 70 80

a commercially attractive synthesis of carboxylic acids.

- We have found, however, that carboxylic acids can be directly obtained by the simultaneous contacting of an olefin, carbon monoxide and oxygen if the reaction is initiated and maintained under substantially anhydrous conditions. During the reaction, the platinum

group metal is reduced from its highest valency state to a lower valency. The reduced metal is then oxidized to the higher valency by contacting of the liquid with oxygen. Preferably, a suitable redox agent is employed to facilitate the oxidation. The overall reaction is as follows:



- wherein  $R_1$ ,  $R_2$  and  $R_3$  are hydrogen, alkyl or alkenyl groups so as to form an olefin as hereinafter described and the catalyst employed is a platinum group metal with, optionally, quantities of a redox agent. The reaction is performed under liquid phase conditions with a solvent comprising an organic solvent of the type hereinafter described.

- The reaction can be performed under relatively mild conditions and exhibits an attractive rate at temperatures from 30° to 300°C. and pressures sufficient to maintain liquid phase conditions. Preferably pressures between atmospheric and 200 atmospheres are employed, the higher pressures being favored to accelerate the reaction. To initiate the reaction under substantially anhydrous conditions, a suitable dehydrating agent is introduced into the reactants, e.g., to introduce an acid anhydride such as acetic anhydride, an acyl halide such as acetyl chloride, a solid inorganic acid anhydride such as boric anhydride or a dehydrated crystalline aluminosilicate molecular sieve, to insure that the reaction will favor the oxidative carbonylation. It is important that the reaction be initiated and maintained under anhydrous conditions, e.g. with reaction solvents containing less than one weight percent of water to insure that the oxidative carbonylation will occur and that undesired reactions such as oxidation to carbon dioxide, aldehydes, ketones or unsaturated esters do not occur.

- To initiate the reaction under anhydrous conditions, we prefer to add the salts, hereafter specified, in their anhydrous state. It is of course apparent that when hydrated salts are employed, an anhydrous reaction medium can be achieved by elimination of the water, e.g., by volatilization of the water by heating stripping or distilling. The distillation can be facilitated in accordance with the skill of the art by use of a suitable water-azeotroping agent such as alkyl esters, e.g., vinyl acetate, ethyl acetate and propyl propionate.

- Spurious side reactions such as might form a carbonyl or unsaturated ester from the olefin, e.g., acetaldehyde or vinyl acetate from ethylene, acetone from propylene, methyl ethyl ketone from butene-1, or that lead to the formation of carbon dioxide, as well as other side reactions can result in the formation of

water. As previously mentioned, the reaction should be maintained under anhydrous conditions, i.e., preferably in the absence of even slight amounts of water. Any slight amounts of water can be eliminated from the system by addition of a suitable dehydrating agent thereto. Substantial quantities of the dehydrating agent are not necessary because water is not formed in the desired oxidative carbonylation reaction, but rather is generated only by the undesired and minor side reactions previously mentioned. Accordingly, we prefer to maintain anhydrous conditions by the addition of from 0.1 to 50, preferably from 2 to 20, and most preferably from 5 to 15 weight percent of an organic dehydrating agent. In general, any organic compound which itself is inert to the oxidative carbonylation and which reacts with water to form under the oxidation conditions a product which does not inhibit the production of the desired acids can be used. For ease of handling, such an agent preferably has from 2 to 25 carbons. Examples of suitable compounds are: acid anhydrides of alkane and benzene carboxylic acids, e.g., acetic, propionic, butyric, valeric, caproic, caprylic and capric anhydride, phthalic anhydride and benzoic anhydride, acyl halides, preferably chlorides, of alkanolic and benzene carboxylic acids such as acetyl chloride, propionyl bromide, caproyl chloride and benzoyl chloride. Another suitable dehydrating agent is a solid inorganic acid anhydride, such as boric anhydride, which can be added to the reaction medium in the same concentrations as indicated for the organic dehydrating agent. The boric acid can be separated from the crude reaction product and dehydrated for recycling to the reaction zone.

Dehydrated molecular sieves can also be used in the aforementioned amounts to provide and maintain anhydrous reaction conditions.

As used herein, the term molecular sieve is meant to comprise crystalline aluminosilicates or zeolites which are either naturally occurring or synthetic compositions of alumina and silica having a crystalline structure, a characteristic x-ray diffraction pattern, and a relatively uniform pore size from 4 to 13 Angstrom units. Based on their ability to preferentially adsorb various compounds within

the pores, these materials have come to be known as molecular sieves.

The preparation of synthetic molecular sieves is a well established art; see British Specification Nos. 777,232 and 777,233 wherein a method of preparation is set forth comprising the mixing of sodium silicate, sodium aluminate and sodium hydroxide to form a gel. The gel is then maintained at a temperature between 100° and 160°C. to induce crystallization of the solid therefrom, then filtered, washed and pelleted or compacted to the desired form. The solid is then calcined at a temperature from 200° to 500°C. to dehydrate the solid and form an active molecular sieve. The sodium cations associated with the molecular sieve can be replaced with different cations by washing with an aqueous solution of a soluble salt of the other cation to base exchange all or a portion of the sodium with one or more of the chosen cations, e.g., hydrogen, ammonium, lithium, potassium, calcium, magnesium, silver, zinc, nickel, strontium, palladium, platinum, iron and cobalt. A description of the base exchange procedure can be found in the afore-said patents.

Any of the naturally occurring or synthetic molecular sieves which are inert to the reaction medium and the oxidation conditions employed in our oxidative carbonylation can be employed. Preferably, zeolites having a silica to alumina molecular ratio of at least 3 and most preferably greater than 5 are employed to insure that the molecular sieve is inert toward the carboxylic acid generally employed as the reaction solvent and toward halogen acids formed on reduction of the redox system. Examples of suitable naturally occurring zeolites having the aforementioned silica to alumina ratios are: ptitilolite, mordenite, laumontite, ferrierite, erionite, epistilbite, stilbite, heulandite, dachriardite and harmontone. Various synthetic zeolites having ratios of silica to alumina greater than about 5 are: zeolite S, zeolite Y, zeolite Z and zeolite T.

The dehydrated molecular sieves can be readily achieved from the hydrated form by heating the latter to temperatures from 200° to 500°C. The regeneration of molecular sieve to a dehydrated condition can be effected in three steps of: heating, purging and cooling. The solid can be heated to temperatures from 200° to 500°C., preferably from 250° to 450°C. and the water removal can be facilitated by purging the solid with an inert gas, air and nitrogen, having a dew point less than 80°F. and preferably less than 50°F. The heat for regeneration can be supplied indirectly or the purge gas can serve as the heat transfer medium, as desired. After desorption of water, generally achieved in 10 minutes to 6 hours, the solid can be cooled by blowing a cool, inert and dry gas

into contact with the solid. Upon cooling to the reaction temperature or lower, the solid can then be introduced into the reactor. In this manner, the process of our invention can be operated with continuous reusing of the dehydrating solid.

Preferably, the dehydrating agent is judiciously selected so that the product of its reaction with water is the same as the reaction solvent. Thus, when acetic acid is the reaction solvent, ketene, an acetyl halide and acetic anhydride are the best chosen dehydrating agent; with propionic acid, either a propionyl halide or propionic anhydride, are best.

Examples of useful olefins are the aliphatic hydrocarbon olefins having from 2 to 12 carbons such as ethylene, propylene, butene-1, butene-2, pentene-2, 2-methylbutene-1, hexene-1, octene-3, 2-propylhexene-1, decene-2, 4,4-dimethylnonene-1, dodecene-1, 6-propyldecene-1, tetradecene-5, 7-ethyldecene-3, hexadecene-1, 4-ethyltridecene-2, octadecene-1, 5,5-dipropyldodecene-3 and eicosene-7. Of these the aliphatic hydrocarbon olefins having from 2 to 8 carbons are preferred. Also preferred are the alpha olefins since these olefins having an unsaturated terminal carbon are more reactive than the other olefins.

As previously mentioned, the reaction is performed under liquid phase conditions in the presence of a liquid organic solvent which has a solvency for the catalyst and which, preferably, is inert to the reaction conditions. Various organic liquids can be employed for this purpose such as sulfones, amides, ketones, ethers and ester. Carboxylic acids such as the lower molecular weight aliphatic acids are preferred solvents and even when another solvent is used, it is preferred to maintain at least 10 percent of the solvent as an aliphatic carboxylic acid.

Illustrative of the preferred solvents are acetic, propionic, butyric, pentanoic, hexanoic, heptanoic, octanoic, pivalic, acrylic and beta-acetoxypionic. Of these, the aliphatic carboxylic acids having from 2 to 6 carbons are preferred. The carboxylic acids are not entirely inert under the oxidation conditions in that the carboxylic acids add to the olefin double bond to form beta-acyloxy compounds. These materials, however, can be readily pyrolyzed to recover both the carboxylic acid for reuse as the reaction medium and the desired unsaturated acid.

Another class of organic solvents that have sufficient solvency for the catalyst salts and that are inert to the oxidative carbonylation and which can be used in lieu of up to 90 percent of the aforementioned carboxylic acids are various amides such as formamide, dimethyl formamide, ethylisopropyl formamide, acetamide, N-phenyl acetamide, N,N-dipropyl a cetamide, iso-butyramide, N-ethyl iso-

butyramide, isovaleramide, N,N-n-caprylamide and isoundecyclamide.

5 Various alkyl and aryl ketones can also be employed in the reaction solvent, e.g. acetone, methylethyl ketone, diethyl ketone, diisopropyl ketone, ethyl n-butyl ketone, methyl n-amyl ketone, cyclohexanone and di-iso-butyl ketone.

10 Various esters can also be employed in the solvent, e.g., ethyl formate, methyl acetate, ethyl acetate, n-propyl formate, iso-propyl acetate, ethyl propionate, n-propyl acetate, sec-butyl acetate, iso-butyl acetate, ethyl n-butyrate, n-butyl acetate, iso-amyl acetate, n-amyl acetate, ethyl formate, ethylene glycol diacetate, glycol diformate, cyclohexyl acetate, furfuryl acetate, iso-amyl n-butyrate, diethyl oxalate, isoamyl isovalerate, methyl benzoate, diethyl malonate, valerolactone, ethyl benzoate, methyl sebacylate, n-propyl benzoate, n-dibutyl oxalate, n-butyl benzoate, diiso-amyl phthalate, dimethyl phthalate, diethyl phthalate, benzyl benzoate and n-dibutyl phthalate.

25 As previously mentioned, the reaction medium should contain catalytic amounts of a platinum group metal. The platinum group metal is of the palladium sub-group or the platinum sub-group, i.e., palladium, rhodium or ruthenium or platinum, osmium or iridium. While all of these metals are active for the reaction, we prefer palladium because of its demonstrated greater activity. The platinum group metal can be employed in amounts between 0.001 and 5 weight percent of the liquid reaction medium; preferably between 30 0.04 and 2.0 weight percent. The platinum group metal can be added to the reaction medium as a finely divided metal, as a soluble salt or as a chelate. Preferably, the metal in its most oxidized form, i.e., as a soluble salt or chelate, is introduced into the reaction zone to avoid the formation of undesired quantities of water. Examples of suitable salts are the halides and carboxylates of the metals such as 45 palladium chloride, rhodium acetate, ruthenium bromide, osmium propionate, iridium benzoate and palladium isobutyrate.

To facilitate the rate of oxidation by rendering it more facile to oxidize the reduced form of the platinum metal, we prefer to employ a reaction medium that contains a halogen, i.e., a bromine or chlorine (preferably a chlorine) containing compound. The halogen can be added as elemental chlorine or bromine; however, it is preferred to employ less volatile halogen compounds such as hydrogen, 50 alkali metal or ammonium halide, e.g., hydrogen chloride; hydrogen bromide, caesium chloride, potassium bromide, sodium bromate, lithium chlorate; ammonium bromide and ammonium chloride. Also, any of the aforementioned platinum group metals can be added to supply a portion of the bromide or chloride and, when the hereafter mentioned 65 multivalent metal redox salts are employed,

these too can be added as the chloride or bromide. A particularly attractive source of halide comprises the acyl halides which, as previously mentioned, also serve as organic 70 dehydrating agents. Thus, the use of acetyl chloride serves to remove any undesired water and also provides a continuous source of hydrogen chloride, thereby replacing any chloride lost during the reaction by vaporization or side reactions. 75

In general, sufficient of any of the aforementioned halogen containing compounds can be added to provide between 0.05 and 5.0 weight percent free or coordinately bonded or covalently bonded halogen in the reaction zone; preferably concentrations between 0.1 and 3.0 weight percent are employed. This amount of halogen is preferably also in excess of the stoichiometric quantity necessary to form the halide of the most oxidized state of platinum group metal, e.g., in excess of two atomic weights of halogen per atomic weight of palladium present. In this manner, a rapid oxidation can be achieved. 85

As previously mentioned, various redox compounds can optionally be used in the reaction medium to accelerate the rate of reaction. In general, any multivalent metal salt having an oxidation potential higher, i.e., more positive than the platinum metal in the solution can be used. Typical of such are the soluble salts of the multivalent metal ions such as the carboxylates, e.g., propionates, benzoates and acetates; nitrates; halides, e.g., bromides and chlorides; of copper, iron, manganese, cobalt, mercury, nickel, cerium, chromium, molybdenum or vanadium. Of these, cupric and ferric salts are preferred and cupric salts are most preferred. In general the multivalent metal ion salt is added to the reaction medium to provide a concentration of the metal therein between 0.1 and 10 weight percent, preferably between 0.5 and 3.0 weight percent. 100

Various other oxidizing agents can also be employed to accelerate the rate of reaction. Included in such agents are the nitrogen oxides that function as redox agents similar to those previously described. These nitrogen oxides can be employed as the only redox agent in the reaction medium or they can be employed jointly with one or more of the aforescribed redox metal salts such as a combination of a soluble nitrogen oxide and a cupric redox agent or ferric redox agent. In general, between 0.01 and 3 weight percent of the reaction medium; preferably between 0.1 and 1 weight percent; calculated as nitrogen dioxide can comprise a nitrogen oxide that is added as a nitrate or nitrite salt or nitrogen oxide vapors. The nitrogen oxides can be added to the reaction medium in various forms, e.g., nitrogen oxide vapors such as nitric oxide, nitrogen dioxide and nitrogen tetroxide, can be introduced into contact with the reaction 130

medium during the oxidation to fix the aforementioned nitrogen oxide content therein or soluble nitrate or nitrite salts such as sodium nitrate, lithium nitrate, lithium nitrite, potassium nitrate and caesium nitrate, can be added to the reaction medium.

5 The process is operated wherein the platinum group metal and redox agent participate in a catalytic manner. In this method, oxygen is introduced together with the olefin and carbon monoxide into contact with the liquid reaction medium. The carbonylation of the olefin and oxidation to the carboxylic acid results in the stoichiometric reduction of the platinum group metal. The introduction of oxygen serves to reoxidize the reduced metal to its more oxidized and active form. This oxidation is known to form a stoichiometric quantity of water. Surprisingly, however, we discovered that so long as we exercised care in initiating the reaction under anhydrous conditions, the water so formed did not promote the more expected but less desired reactions, i.e., formation of an aldehyde or ketone from the olefin or oxidation of carbon monoxide to carbon dioxide, but rather, the water so formed was consumed in formation of the desired acid product so that no accumulation of water resulted during the reaction. Accordingly, in accordance with our discovery, the reaction can be maintained under anhydrous conditions and a preparation of alpha,beta-unsaturated or beta-acyloxy-carboxylic acids is achieved without need to continuously add a dehydrating agent or to strip the water from the reaction zone.

10 The oxygen is introduced into contact with the liquid reaction medium at a rate controlled in response to the oxygen content of the exit gases from the reaction zone. Continuous or intermittent introduction of oxygen can be employed; however, continuous introduction is preferred. Preferably, the rate of oxygen introduction is controlled relative to the olefin and carbon monoxide rates so as to maintain the oxygen content of the exit gases below the explosive concentration, i.e., less than 10 and preferably less than 3 volume percent. Under these conditions, the excess gas comprising chiefly the olefin and carbon monoxide can be recycled to the liquid reaction medium. When the olefin is a liquid under the reaction conditions, an inert gas such as nitrogen, air or mixtures of nitrogen and air can be employed to dilute the gas phase and exit gas stream from the reactor and thereby avoid explosive gas compositions.

15 The carbon monoxide is introduced into contact with the reactants at a sufficient rate to insure that the desired carbonylation occurs. Relative ratios of the carbon monoxide based on the olefin can be from 1:10 to 10:1 molecular units per molecular unit of olefin, preferably rates from 1:1 to 5:1 and most pre-

ferably from 1:1 to 2:1 molecular ratios are employed. 65

The reaction can be performed under relatively mild conditions, e.g., temperatures from 30° to 300°C.; preferably from 90° to 200°C. are employed. The reaction pressure employed is sufficient to maintain a liquid phase and preferably, when gaseous olefins are employed, superatmospheric pressures are used to increase the solubility of the olefin in the reaction medium and thereby accelerate the reaction rate. Accordingly, pressures from atmospheric to 200 atmospheres or more, preferably elevated pressures from 10 to 100 atmospheres are used. 70 75

During the oxidation, a portion of the liquid reaction medium can be continuously withdrawn and distilled to recover the desired products from the reaction medium which contains the catalyst salts and which is recycled for further contact to the reaction zone. Preferably, care is exercised to remove any quantities of water from this recycle reaction. The removal of the water from this recycle stream can be facilitated by azeotropic distillation, e.g., by the addition of a suitable water azeotrope forming agent to remove all water in the distillation and/or by the addition of any of the aforementioned organic dehydrating agents to the reaction medium, e.g. acetic anhydride, phthalic anhydride and acetyl chloride, to the recycle stream. 80 85 90 95

In the preparation of acrylic acid with an acetic acid-acetic anhydride reaction system, some difficulty is encountered in separating the acrylic acid product since acetic anhydride has an almost identical atmospheric boiling point temperature. This can be obviated by performing the oxidation to deplete the product of all acetic anhydride or by adding water to the crude product to hydrolyze the acetic anhydride to acetic acid. 100 105

The problem can also be obviated by use of any of the aforementioned higher boiling organic dehydrating agents or by use of the solid inorganic dehydrating agents which can be removed from the product by filtration. 110

Frequently, however, it is desired to use acetic anhydride, particularly since the most attractive oxidation rates are achieved with this agent. The acetic anhydride can be used without the necessity to hydrolyze the excess anhydride remaining in the product if a high boiling carboxylic acid is also included in the reaction solvent. Examples of high boiling carboxylic acids include butyric, isobutyric, valeric, isovaleric, caproic and pivalic. The reaction product from the oxidation thereby contains: acetic acid, acetic anhydride, acrylic acid, beta-acetoxypionic acid and one of the aforementioned high boiling carboxylic acids. The distillation of this product will not remove acetic anhydride overhead since this anhydride reacts with the high boiling carboxylic acid to form acetic acid and the an- 115 120 125

hydride of the high boiling acid. Because the acrylic acid is more volatile than the anhydride of the high boiling acid, the acrylic can be recovered in high purity as a distillate. To insure complete removal of the acetic anhydride, from two to ten molecular weights of the high boiling acid should be provided for each molecular weight of acetic anhydride.

After distillation of the acrylic acid the distillation residue can be combined with acetic acid and recycled to the reaction zone. The addition of acetic acid provides a source of acetic anhydride for the oxidation since the anhydride of the high boiling acid reacts with acetic acid to yield acetic anhydride and the high boiling acid.

The following examples will illustrate the practice of our invention and serve to demonstrate the results obtainable thereby:

#### EXAMPLE 1

Into a half-gallon autoclave was placed 1 gram palladium chloride, 10 grams anhydrous cupric chloride, 100 grams acetic anhydride, 400 grams acetic acid and 153 grams propylene. The autoclave was pressured with carbon monoxide to 500 psig and then heated to 300°F. While maintaining this temperature, and stirring, oxygen was slowly introduced into contact with the reactants at 20 psi increments to maintain a relatively constant pressure. After thirty minutes, the introduction of oxygen was ceased and the autoclave cooled, depressured and opened. The liquid contents were removed and distilled to recover, as the major product, a 40 gram fraction boiling at 80°—85°C. at 2—3 millimeters Hg pressure. This compound, which solidified on standing, was dissolved in aqueous methanol and crotonic acid, having a melting point of 72°C. was recrystallized therefrom. The equivalent weight of the solid determined by base neutralization was 87.2 grams per equivalent of base, indicating a high degree of purity of the product.

The experiment was repeated with a reaction medium comprising 480 grams acetic acid and 20 grams acetic anhydride and the major product obtained was 75 grams beta-acetoxybutyric acid.

#### EXAMPLE 2

Into a half-gallon autoclave was placed 1 gram palladium chloride, 10 grams anhydrous cupric chloride, 400 grams acetic acid and 100 grams acetic anhydride. The autoclave was pressured to 300 psig with ethylene, then to 500 psig with carbon monoxide and thereafter heated to 300°F. Oxygen was introduced at twenty psi increments over a thirty-minute period. After thirty minutes, the autoclave was cooled, depressured and opened. The solution was distilled to recover 45 grams of product boiling at 119°C. at 2.5 millimeters Hg pressure. This product had a neutralization

equivalent of 131.2 grams per equivalent and a density at 22°C. of 1.4315, corresponding quite closely to those of beta-acetoxypropionic acid. A sample of this acid was passed into contact with glass beads at 300°C. in a glass tube. The product was collected in an ice water trap and inspected by gas chromatographic analysis to find the entire product to be an equimolar mixture of acetic and acrylic acids

#### EXAMPLE 3

A half-gallon autoclave was charged with 1.0 gram palladium chloride, 5 grams lithium chloride, 5 grams anhydrous cupric chloride, 500 grams acetic acid and 50 grams acetic anhydride. The autoclave was pressured with 300 psi of ethylene, then with an additional 600 psi of carbon monoxide, and thereafter heated to 300°F. While maintaining this temperature and stirring, oxygen was introduced in 10—20 psig increments over a twenty-minute period. Then the autoclave was cooled, depressured into a gas receiver and opened. The liquid product was distilled and analyzed by gas chromatography to find about 78 grams of a mixture of acrylic and beta-acetyloxypropionic acid corresponding to a yield of acrylic acid of 66.6 grams. The collected gases from the autoclave were analyzed and found to contain only 1.67 mol percent of carbon dioxide, indicating a high efficiency of the oxidation.

The example was repeated, but in lieu of palladium chloride, 1 gram of chloroplatinic acid and 1 gram of rhodium chloride were substituted therefore in two separate experiments. Substantially the same results were obtained.

The example was also repeated, except 5 grams of 70 percent nitric acid were used in lieu of the cupric chloride. The reaction rate was slower than observed when using cupric chloride, but a continuous reaction nevertheless occurred.

When the experiment was repeated but without precaution to provide and maintain an anhydrous reaction medium, about 40 grams of acetaldehyde were obtained as the major liquid product.

#### EXAMPLE 4

Example 3 was repeated with the same amounts of salts but with a reaction medium comprising 20 parts acetic anhydride and 400 parts acetic acid. The autoclave was heated to 100°C. and pressured to 400 psig with ethylene, then to 800 psig with carbon monoxide. Oxygen was added in ten 20 psi increments over a one-hour period while stirring and maintaining the temperature at 100°C. The final pressure at 100°C. was 550 psig. The autoclave was then cooled, depressured and opened. The liquid contents were distilled to recover 49 grams beta-acetoxypropionic



acid, boiling at 106°—107°C. under 1 millimeter Hg pressure with a refractive index at 28°C. of 1.4293 and 8 grams of acrylic acid.

- 5 The example 3 was repeated with the same amounts of salts but with a reaction medium comprising 50 grams acetic anhydride and 400 grams dimethyl formamide. The autoclave was pressured as in Example 4 and then heated to 120°C. The initial pressure was 910 psig and, after ten oxygen additions of 20 psi increments each over a one-hour period, the final pressure was 860 psig. Beta-acetoxypionic acid was recovered as a product.

#### EXAMPLE 5

- Into a 1/2 gallon autoclave were placed 1 gram palladium chloride, 5 grams lithium chloride, 5 grams lithium acetate dihydrate, 5 grams cupric chloride and 90 grams of sodium mordenite which had been calcined for 15 hours at 700°F. To the reactants were added 500 grams of acetic acid and the autoclave was then pressured to 450 psig with ethylene and then to 900 psig with carbon monoxide. The reactants were heated to 280°F. and oxygen was slowly introduced in small increments during a 10-minute reaction period. After completion of the reaction the autoclave was cooled and opened and the contents thereof were filtered to separate the solid sodium mordenite from the liquid products and reactants. The liquid filtrate was distilled to separate the acetic acid and recover 14 grams of acrylic acid and 43 grams of beta-acetoxypionic acid. The oxidation also yielded 2.5 grams of propionic acid and 17 grams of carbon dioxide.

- 40 The reaction was repeated with 103 grams of lithium mordenite in place of the sodium mordenite and 25 grams of acrylic acid and 15 grams of polyacrylic acid with 12 grams of carbon dioxide were produced.

- 45 In repeated experiments, 100 milliliters of the reaction medium was replaced respectively with 100 milliliters of sulfolane and 100 milliliters of o-dichlorobenzene. Comparable yields

of acrylic acid and beta-acetoxypionic acid were achieved in these experiments.

#### EXAMPLE 6

Into a half-gallon autoclave was placed 1 gram of palladium chloride, 5 grams of anhydrous cupric chloride, 5 grams of lithium chloride, 5 grams of lithium acetate dihydrate, and 25 grams of boric anhydride. The autoclave was pressured to 300 psig with ethylene and then to a total pressure of 900 psig with carbon monoxide. The resulting mixture was heated to 300°F., and while maintaining this temperature, and stirring, oxygen was slowly introduced into contact with the reactants at 10 to 20 psi increments to maintain a relatively constant pressure. After 30 minutes, the introduction of oxygen was ceased and the autoclave was cooled, depressured and opened. The reaction product comprised a solid portion and a liquid portion. The solid portion of the product consisting of catalyst residue along with boric acid and boric anhydride was removed from the liquid product by filtration. Fractional distillation of the liquid product produced 3.5 grams of acrylic acid, 26 grams of beta-acetoxypionic acid, and 8 grams of propionic acid.

#### Fractional Distillation of Crude Products

A typical crude product from the oxidative carbonylation of ethylene to acrylic acid in an acetic acid-pivalic acid solvent was distilled in a 30-plate Oldershaw column at 22—26 millimeters Hg pressure and a reflux ratio of 7:3. One gram of hydroquinone and one gram of copper metal were added to the distillation flask to inhibit polymerization of the acrylic acid. The crude product had the following composition:

Component	Grams
acetic acid	55
anhydride (calculated as acetic)	100
acrylic acid	100
pivalic acid	200

The following distillates and residues were obtained:

Distillate	Boiling Point	Composition (grams)
1	34°C	70 acetic acid
2	33	32 acetic acid
3	33	50 acetic acid
4	34—54	26 acetic/25 acrylic
5	55—57	41 acrylic
6	58—76	23 acrylic/21 pivalic
Residue	—	6 pivalic anhydride
		150 pivalic anhydride

#### EXAMPLE 7

- To a one-gallon autoclave were charged 450 grams pivalic acid, 50 grams acetic acid, 50 grams acetic anhydride, 1 gram palladium chloride, 5 grams lithium chloride and 5 grams

cupric chloride dihydrate. The autoclave was pressured to 300 psig with ethylene and then to 900 psig with carbon monoxide. The mixture was heated to 300°F. and oxygen and nitrogen were slowly added during a thirty-

minute period. The reaction product was distilled under vacuum in a similar method to that described above to recover 5 grams acrylic acid and 41 grams beta-acetoxypionic acid.

5

#### EXAMPLE 8

To a one-gallon autoclave were charged 800 grams pivalic acid, 150 grams acetic anhydride, 50 grams acetic acid, 1 gram palladium chloride, 5 grams lithium chloride, 3 grams lithium acetate and 5 grams cupric chloride dihydrate. The mixture was analyzed for total anhydride and found to contain 133 grams calculated as acetic anhydride. The autoclave was pressured to 450 psig with ethy-

lene, then to 900 psig with carbon monoxide and heated to 280°F. Oxygen was added in 20 psi increments during a twenty-minute period while nitrogen was added to maintain a constant pressure.

The autoclave was cooled and depressured and the liquid products analyzed for anhydride. The total anhydride present in the product was 42 grams calculated as acetic anhydride. A 606-gram fraction of the crude product was distilled in a 30-plate Oldershaw column at 24 millimeters mercury pressure and a reflux ratio of 85 parts per 15 parts distillate. The following distillates were obtained:

	Distillate	Boiling Range	Composition
30	1	31—35°C.	62 grams acetic acid
	2	35.5—57°C.	40 grams acetic acid/2 g. unidentified
	3	57—75°C.	22 grams acrylic/22 grams pivalic
			4 grams unidentified
35	4	75°C.	6 grams acrylic/31 grams pivalic
	5	75—78°C.	8 grams acrylic/60 grams pivalic
	6	78—81°C.	262 grams pivalic
	Residue	—	71 grams

#### WHAT WE CLAIM IS:—

1. The manufacture of carboxylic acid products comprising alpha- beta-ethylenically unsaturated carboxylic acids and/or beta-acyloxy carboxylic acids by the oxidative carbonylation of hydrocarbon olefins that comprises contacting said olefins, oxygen and carbon monoxide under anhydrous conditions with an anhydrous organic reaction medium comprising an aliphatic carboxylic acid solvent and from 0.001 to 5.0 weight percent of a platinum group metal as hereinbefore defined at a temperature between 30° and 300°C. and sufficient pressure to maintain said solvent in liquid phase.

2. The manufacture according to claim 1 wherein the reaction medium contains a dehydrating agent.

3. The manufacture according to claim 2 wherein the reaction medium contains acetic acid, a carboxylic acid having a boiling point in excess of the boiling point of said alpha, beta-ethylenically unsaturated acids and the anhydrides of said acids.

4. The manufacture according to claim 2 wherein the said dehydrating agent is a dehydrated aluminosilicate zeolite.

5. The manufacture according to any of

the preceding claims wherein the reaction medium also contains as a redox agent a soluble nitrogen oxide salt and/or a soluble salt of a multivalent transitional metal having an oxidation potential in the solution more positive than the platinum group metal.

6. The manufacture according to claim 5 wherein the redox agent is a soluble copper salt.

7. The manufacture according to any of the preceding claims wherein the olefin is ethylene, the carboxylic acid products are acrylic acid and beta-acetoxypionic acid.

8. The manufacture according to claim 2 wherein the solvent is acetic acid and the dehydrating agent is acetic anhydride.

9. The manufacture according to any of the preceding claims wherein the platinum group metal is palladium.

10. The manufacture of carboxylic acid products comprising alpha, beta-ethylenically unsaturated carboxylic acids and/or beta-acyloxy carboxylic acids substantially as herein described.

STEVENS, LANGNER, PARRY &  
ROLLINSON,

Chartered Patent Agents,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1967.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained